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METAL PLATING WASTES IN MUNICIPAL SEWERAGE SYSTEMS

F.W. Kittrell

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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F. W. Kittrell, Public Health Engineer
Robert A. Taft Sanitary Engineering Center
Public Health Service
Cincinnati, Ohio

The subject of metal plating wastes in sewage and their effects on treatment is a complex one. This complexity is reflected in the frequent contradictions on the subject in the technical literature.

The wastes include oils and greases, detergents, acids and alkalies, cyanide and other less toxic radicals, a dozen or more metals with varying degrees of toxicity, and an almost infinite variety of patented additive compounds of highly secret composition.(1) Their rate of discharge from the plating plant is highly irregular both in flow and in combinations and concentrations of constituents. Cyanide, for example, normally may vary between 20 and 100 ppm in wastes from rinsing operations, but may increase suddenly to many thousand ppm when a plating bath is dumped.(2) The biological effects of each of the toxic constituents can vary widely. Toxicity may be influenced by

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the chemical composition of the toxic material, its capacity for ionization, the pH of the solution, the synergistic effects of other constituents, and the degree of acclimatization of biological forms to the material.

It usually is extremely difficult, and may be impossible, to identify and assess the effects of any individual constituent when plating wastes cause problems at a sewage treatment plant. Most of the information in the literature on effects has been obtained from laboratory or controlled, small, pilot plant observation.

PLATING WASTE COMPLEXITIES

Cyanide

The toxicity of cyanide is affected by a variety of factors. It is related to the degree to which the compound dissociates to yield the CN^- ion. (3) The simple cyanides of sodium, potassium, cadmium, and zinc dissociate readily and are extremely toxic. The complexes of nickel, copper, and iron may dissociate only slightly, and are much less toxic. Treatment of cyanide waste with iron salts, to render them relatively nontoxic before discharge to streams, has been employed in practical waste disposal. It has been suggested that low concentrations of the simpler cyanides can be rendered nontoxic by the addition of nickel which itself is toxic.(3) The addition of cyanide to toxic solutions of copper forms the cuprous cyanide complex which is less toxic than either of these two toxic materials alone.

The foregoing comments assume a pH in the alkaline range of about 8.0 or higher. As pH values decrease dissociation to yield CN^- increases rapidly. Nickelocyanide is about 1,000 times as toxic at pH 6.5 as it is at 8.0. At 6.5 its toxicity approaches that of the simpler cyanides.(3)

Opportunity for biological systems to become acclimatized to cyanide enormously affects their capacity to tolerate this material. As little as 2 ppm of CN, as sodium- or potassium cyanide, inhibited nitrification in an experimental trickling filter treating sewage when first applied. After a week of continuous application of 2 ppm CN the filter performance returned to normal.(4) Further operation with successively increasing concentrations of CN resulted in tolerance of the filter to as much as 200 ppm of CN. A filter properly acclimatized to 100 ppm of CN, from potassium-, zinc-, cadmium-, or copper cyanide, produced an effluent containing only 1 ppm of CN. At least half of the cyanide N appeared in the effluent as ammonia, nitrate or nitrite. This indicated that the acclimatized trickling filter bacteria were using some of the cyanide as food rather than being destroyed by its potential toxicity. The other half of the cyanide N was not accounted for, and it was suggested that it may have evolved as nitrogen gas, accumulated in the filter slimes, or left the filter as cyanates in the effluent.(4)

The sewage in the foregoing experiments was gradually replaced with tap water until the filters were receiving only tap water containing

100 ppm of CN. The bacteria continued to feed on the cyanide, accomplishing almost complete destruction of the simpler cyanides and 75 to 80 per cent of the complexed cyanides.

Chromium

After cyanides, chromium is the next most important waste from the plating industry. An understanding of its highly complex chemistry is important in chromium recovery by ion-exchange.(5) When dealing with chromium in a sewerage system or stream, however, it is necessary only to distinguish between the hexavalent and trivalent forms. Soluble hexavalent chromium is about 100 times as toxic as the relatively insoluble trivalent form.(6)

Hexavalent chromium is used for plating, but there is some conversion to the trivalent form in the baths. Most of the chromium wasted to the sewer is hexavalent. Hexavalent chromium is reduced to trivalent in the presence of organic matter in sewage. Presumably this reaction proceeds more rapidly if the sewage is septic, but it has been stated that, in practice, most of the hexavalent chromium discharged to sewers probably is in the trivalent form on arrival at sewage plants.(6) It is reported that hexavalent chromium cannot exist in anaerobic sludge digesters, but is rapidly converted to the less toxic trivalent form.

EFFECTS ON AND LIMITS FOR ADMISSION TO SEWERAGE SYSTEMS

There is fair agreement among municipal and other authorities on limitations that should be imposed on plating wastes admitted to public sewers. The ranges of limits suggested or in actual use are narrower than might be expected in view of the complexities of plating wastes and their effects on sewerage systems.

Collection System

Physical damage to the collection system may result from the strong acids and alkalis used in cleaning, pickling, stripping and otherwise preparing metals for plating, and in the plating baths themselves. Protection against corrosive damage is included in most sewer ordinances by limitations on pH of industrial wastes. Many of the lower limits established are from 5.0 to 5.5, (7)(8) though as low as 4.5 has been accepted.(9) Upper limits are 9.0 to 10.0(10) with 9.0 to 9.5 being the more commonly used values. At least one ordinance requires that the average daily pH shall be 7.0.(10) These limits help to prevent inhibition of biological activity at the treatment plant as well as prevent physical damage to the sewers.

Metals must be scrupulously cleansed of oil and grease before plating, and this is an important preliminary process in most plating plants. In the majority of plants the quantities of oil and grease involved are small, and clogging of sewers rarely occurs. The usual sewer ordinance restrictions on oils and greases will protect against

excessive quantities of these materials. Maximum limits of 50 to 100 ppm have been suggested for oil and grease, with mineral oil excluded or removed to the maximum degree possible before discharge.(7)(8)

Numerous references are made to the possibility of reaction between acid and cyanide wastes in sewers that will liberate hydrogen cyanide gas and create a hazard to sewer maintenance crews. This is a definite possibility, but no report that it has occurred and no limit imposed on cyanide in sewers because of this has been found in sewer ordinances. Limits of 20 ppm of cyanide in small sewers and 10 ppm in large sewers, where men may work, have been suggested.(11)

Primary Sedimentation

Plating wastes that will not corrode or clog sewers or liberate hydrogen cyanide gas in them should not affect primary sedimentation adversely. Some of the metals, especially trivalent chromium, can coagulate and assist sedimentation of sewage solids.

The effect of primary sewage treatment on plating wastes depends largely on the forms in which the constituents arrive at the treatment plant. Insoluble oils and greases will be reduced, but soluble oils and greases will be little affected.

Chromium that remains hexavalent will pass through the sedimentation process. Chromium arriving in the trivalent form or converting to trivalent in the primary tank will settle out almost completely.(12)

Cyanides and the metals associated with them do not settle unless they have received pretreatment at the plating plant which renders them

insoluble. At least one large city permits discharge of certain plating wastes pretreated to eliminate cyanide but without settling of the metals precipitated in the process. The metals, usually in the hydroxide or carbonate form, settle almost completely in the primary sedimentation basin.

If pretreatment of cyanide wastes at a plating plant is incomplete, metallic cyanides also may settle in the primary basin at the sewage plant. The cyanides of most of the plating metals are not soluble in water. They are held in solution in plating baths by the addition of sodium- or potassium cyanide, which is called free cyanide. If insufficient oxidizing agent to destroy all cyanides is used, the free cyanide is attacked first. The unoxidized heavy metal cyanides precipitate and settle. Even when theoretically sufficient oxidizing agent is applied some metallic cyanide may escape the pretreatment process if mixing and contact facilities are not properly designed or operated. This applies especially to nickelocyanide and to a lesser extent to cuprous cyanide, which resist oxidation. It is not so likely to occur with zinc and cadmium cyanides, which are more easily oxidized.

The only limits on plating waste constituents necessary for protection of the primary treatment process are those for pH, oils and greases. If primary treatment only is employed, the limits imposed may be those necessary to protect the receiving stream and the sludge digestion process. Limits for the latter purpose will be discussed later.

For protection of the receiving stream only, limits for toxic constituents in the raw sewage of a primary sewage treatment plant may be based on permissible limits in the receiving stream after mixing and dilution. One set of limits for stream water used as a guide by

several states includes the following:(13)

Cyanide (CN)	Substantially none
Copper (Cu)	0.3 ppm
Chromium (Cr-Hexavalent)	0.05 ppm
Cadmium (Cd)	0.4 ppm
Zinc (Zn)	0.3 ppm
Nickel (Ni)	2 ppm

If hexavalent chromium is absent and dilution of the treated sewage in the receiving stream is as much as 20 to 1, the limits necessary for protection of sludge digestion may take precedence over the above values.

Sludge Digestion

Both cyanides and metals used in plating affect sludge digestion. The effects range from minor reduction of gas production to complete stoppage of digestion.

Insoluble metals that settle in the primary basin are transferred to the sludge digestion tank. In addition, the water accompanying the sludge solids contains any soluble metal carried by the raw sewage. The result is a concentration of the metal in the sludge many times that in the raw sewage. A copper content of 0.5 ppm in sewage was concentrated to over 100 ppm in the sludge, and it was concluded that more than 1 ppm in raw sewage would cause a decrease in efficiency of sludge digestion.(14) It was found also that 200 ppm of chromium in sludge reduced the rate of digestion and that more than 1 ppm in raw sewage had an effect on sludge digestion similar to that of copper.

Although soluble cyanides do not concentrate in sludge as do insoluble metals, very low concentrations in the raw sewage can affect sludge digestion. Only 1.6 ppm of CN, added experimentally to sludge as sodium cyanide, inhibited gas production.(15) With continued additions the sludge rather quickly built up a tolerance to cyanide and resumed normal digestion. The tolerance increased with increasing additions until the sludge handled as much as 16 ppm of CN without adverse effect. The experiment was not carried beyond this point. Presumably higher concentrations of the relatively stable cyanide complexes would have less effect on sludge digestion than sodium cyanide. Apparently sludge can develop the capacity to destroy fairly high concentrations without difficulty if the concentration of cyanide in sewage is maintained at a reasonably constant level. The nature of plating operations is such that a constant level of cyanides can not be assured, and a low limit is set for the raw sewage.

The following maximum values for common metal plating constituents in raw sewage have been reported not to interfere with sludge digestion:(16)

Cyanide (CN)	1 ppm
Copper (Cu)	1 ppm
Chromium (Cr)	5 ppm
Zinc (Zn)	5 ppm

Some city ordinances permit as much as 2 ppm of CN in sewage. Some set more stringent limits on both chromium and zinc, permitting only 3 ppm.

Information on nickel and cadmium is limited. Only one sewer authority was found to have set quantitative limits, which were 10 ppm for nickel and 3 ppm for cadmium.(17) One State health department recommends that municipal ordinances prohibit cadmium in excess of 1 ppm.(18)

Biological Secondary Treatment

Constituents of plating wastes can cause reductions in nitrification and in efficiency of B.O.D. and solids removal in both trickling filter and activated sludge processes. In some cases all biological activity may be stopped.

The reaction of trickling filters to cyanides, and their capacity to develop tolerance to high, constant concentrations have been described in a preceding section. Laboratory experiments have indicated that the activated sludge process reacts similarly. Tolerance to as much as 132 ppm of CN was built up by gradually stepping up the concentration of cyanide. Quantitative decomposition of the organic feed was obtained up to this level.(16) Above this concentration only partial decomposition occurred. With as much as 25 ppm of CN in the feed all cyanide was destroyed, but with higher concentrations cyanide destruction was only partial. At 32 ppm all life higher than bacteria was killed, but the bacteria maintained a very efficient floc up to 132 ppm of CN. The effect on nitrification was not mentioned in the report on these experiments but other research has included observation

of this factor. (19) Nitrification was slightly reduced by as little as 1 ppm CN as sodium cyanide, but was not eliminated by as much as 21 ppm. Suspended solids and settleability were not affected. It was concluded also that appreciable but undetermined quantities of the CN were removed as HCN by the aeration applied to maintain the activated sludge.

Apparently the limits of 1 to 2 ppm CN established for protection of digestion are considered adequate for protection of secondary biological treatment also.

The effect of pretreated plating wastes on sewage treatment has received relatively little attention. Wastes from treating copper and zinc cyanide wastes with lime-sulfur were examined, (15)(19) but this method of treatment has not gained popularity in this country. The effect, on trickling filters, of cyanide treated by alkaline chlorination has been reported.(20) A solution of HCN was treated with an excess of bleaching powder, and the excess chlorine was neutralized. Although not stated specifically, the CN apparently was oxidized only to the cyanate and not to carbon dioxide and nitrogen. This solution was added to settled sewage to give a concentration equivalent to an original CN content of 28.8 ppm. Both settled sewage only and settled sewage with the treated cyanide solution were applied for 103 days to laboratory trickling filters. The B.O.D. of the settled sewage averaged 161 ppm. The average B.O.D. of the effluent from the filter receiving sewage only was 6.4 ppm. That of the effluent from the filter

receiving sewage plus treated cyanide was 12.1 ppm, or very nearly twice as much as for sewage only.

As little as 1 ppm of hexavalent chromium in the applied sewage has been found to affect nitrification in trickling filters, and 2 ppm had a similar effect in the activated sludge process.(21) In terms of overall treatment efficiency, trickling filters appeared better able than activated sludge to resist the effects of chromium. Trivalent chromium is reported to be relatively harmless to nitrification.

Most sewer authorities have not set a quantitative limit on zinc, but at least one has selected 3 ppm,(17) and there is some indication that as much as 5 ppm may be acceptable.(22)

The only limits for cadmium and nickel found are those discussed in connection with sludge digestion.

At least one authority believes a limit is desirable for the sum of all metal ions, excluding the alkaline earth metals but including iron and manganese. In addition to individual limits of 5 ppm for copper and 3 ppm for chromium, he suggests a limit of 30 ppm for the sum of all metals in settled sewage submitted to biological treatment.(23)

Chlorination

Cyanides consume proportionately more chlorine than any other

plating waste constituent where chlorination is a feature of sewage treatment. Each ppm of CN uses between 3 and 7 ppm of chlorine, depending on the extent to which the chlorine demand of the sewage is satisfied. Three to 4 ppm of CN can double the chlorine demand of raw sewage. Where the cyanide is combined with reduced metallic elements, as in nickelous and cuprous cyanides, the metals will react with and use chlorine in stoichiometric quantities. Hexavalent chromium interferes with the determination of chlorine residual. It causes readings higher than true values.

No ordinance establishing limits on specific constituents of plating wastes for prevention of excessive chlorine demand has been found. At least one municipality, however, has set a limit of 15 ppm chlorine demand on any waste discharged to the public sewers. If cyanide waste, for example, is involved, this limits CN to a maximum of 5.5 ppm, since each ppm of CN requires a minimum of 2.73 ppm of chlorine to convert it to cyanate.(22)

CONSIDERATION OF PLATING WASTES IN SEWAGE PLANT DESIGN

It is not economically sound to design sewage plants to provide the special chemical treatment facilities necessary for continuous treatment of plating wastes. It is much cheaper to treat them in the relatively small volumes produced at the plating plants. It is not feasible technically to treat them at the sewage plant when the wastes include both chromium and cyanides. The chromium requires reduction,

while the cyanides must be oxidized.

The design engineer must give first consideration to the treatment needs of the domestic sewage involved. The selection of processes must be based primarily on these needs. Consideration may be given to alternate processes that should be less affected by plating wastes only where there will be no conflict with the basic sewage treatment requirements and where the alternates are not excessively costly. No feasible modifications of processes are known that will substitute for a sound sewer ordinance limiting the concentrations of plating wastes that will be admitted to the system.

Even where such ordinances are in effect, however, it would be unrealistic to ignore the probability that temporary excesses of plating wastes occasionally will enter the sewers of municipalities where there are numerous or large plating plants. If processes can be provided that will accomplish the required sewage treatment and at the same time be less susceptible to damage by occasional excesses of plating wastes, the probability of successful operation during periods of such excesses should be improved.

Information on sewerage systems designed specifically to resist adverse effects of plating wastes was not found in the literature. Data reported in the literature from laboratory and small scale pilot plant research and information obtained by personal communication indicate that there are principles that might be applied to full scale treatment plants to lessen the difficulties caused by temporary

excesses of plating wastes. Most of these principles, however, should be investigated on a larger pilot plant scale before they are translated into plant design.

Collection System

There appears to be relatively little of practical value that the design engineer can incorporate in the collection system to minimize adverse effects of plating wastes.

Plating wastes should discharge into a sewer carrying the maximum flow of sewage available near the plating plant. The dilution afforded by the sewage and its buffering capacity will provide some protection against damage to the sewer line by acid plating wastes. In some cases small acid resistant sewer lines may be justified to carry the wastes to larger sewers where dilution is available. The plating plant should bear any additional cost of such construction.

Presumably time of contact is one factor in conversion of hexavalent chromium to the less toxic trivalent form by the organic matter in sewage. In cases where a choice is practical it appears that potential problems of hexavalent chromium at the sewage plant might be minimized by discharge of such wastes into the longest sewer line available near the plating plant.

Oil and Grease Removal

Oils and greases in plating wastes probably will not require special consideration in design of facilities for removal of these materials.

Chemical Feeders

The cost of chemical feeders for the single purpose of combatting occasional excesses of plating wastes probably is not justifiable. Where chemical coagulation is desirable to accomplish the required degree of sewage treatment the necessary chemical feeders may be useful in emergencies involving certain types of wastes.

A lime feeder will neutralize slugs of acid. It may be used to adjust pH of the sewage to precipitate some of the toxic metals that would interfere with biological oxidation processes.

Conversion of cyanides to the far less toxic ferric ferrocyanide complex by use of ferrous sulfate has been used as one method of cyanide treatment. A ferrous sulfate feeder might aid in minimizing adverse effects of slugs of cyanides on biological oxidation processes.

There does not appear to be any practical method at the primary basin of dealing with slugs of any hexavalent chromium that might reach the treatment plant. Rapid chemical reduction requires a pH in the range of 2.5 to 3.0. Lime and ferrous sulfate applied ahead of the primary sedimentation basin at one small town did not accomplish any reduction in chromium.(24)

Sewage Digestion

Temporary excesses of plating wastes in raw sewage normally should not affect sludge digestion seriously. Reported cases of

interference usually have resulted from prolonged excesses in raw sewage that gradually concentrated in the digester to levels that reduced digestion rates.

Equipment for mixing sludge in the digester should distribute temporary high concentrations of the toxic materials throughout the sludge and avoid localized pockets of maximum interference with digestion.

Only one instance has been found in the literature where plating wastes importantly influenced sewage treatment design decisions.(25) There were 3 large and more than 100 small metal finishing plants in the town involved. The town passed and attempted to enforce a sewer ordinance prohibiting harmful industrial wastes. In spite of this action, sampling and analysis of the sewage revealed concentrations of toxic metal wastes that would render doubtful the success of biological sludge digestion. As a result the consultants recommended non-biologic treatment for the sludge.

Biological Secondary Treatment

Trickling filters appear generally to absorb shock loads of plating wastes slightly better than does activated sludge. Where plating wastes are involved and the higher treatment efficiency of activated sludge is not essential trickling filters probably should be chosen. There is experimental evidence that filters with recirculation rates as high as 10 to 1 can tolerate copper, cyanide, and chromium in

amounts 2 to 5 times as great as those acceptable to standard filters.(23)

There also is evidence that increasing aeration solids in the activated sludge process from about 2,500 ppm to the range of 8,500 to 12,500 ppm will give tolerance to copper at least twice as high as that acceptable with normal solids.(23) It does not appear practical, however, to attempt to apply this principle to present activated sludge processes. The same source states that both conventional trickling filters and activated sludge can build up acquired tolerances to 6 or 7 ppm of chromium and 10 or 15 ppm of copper. Rather surprisingly both types of processes lose efficiency when the toxic metals are suddenly diminished. This is in line with previous comments on the ability of sewage treatment processes to develop tolerances to higher concentrations of some plating waste constituents, provided the concentrations remain at reasonably constant levels. Unfortunately, plating wastes are discharged at highly variable rates. It has been suggested that problems of fluctuating discharges by plating plants, with subsequent variable concentrations at sewage plants, might be minimized by lagooning the wastes and discharging to sewerage systems at controlled rates. Lagoons preferably should discharge to sewers carrying sewage from residential areas which will provide immediate dilution.(26) Such controlled discharge might make it possible for biological sewage treatment plants to treat higher concentrations of cyanides than present practice permits.(27)

It also might make possible treatment of higher concentrations of some of the metals provided the sludge were treated by a non-biologic method.

Final Chlorination

Consideration of chlorinator capacity in excess of that necessary for final chlorination of normal sewage treatment plant effluent may be desirable if cyanide wastes are involved. Frequently, reasonable increases in chlorinator capacity can be achieved with relatively little added cost. If there is a probability that chlorination of fairly high concentrations of cyanide occasionally will be necessary, consideration should be given in design to the possible liberation of irritating and highly toxic cyanogen chloride gas. This is especially apt to result if chlorination takes place at pH as low as 6.5. Mixing devices may be placed outdoors or adequately ventilated.

The foregoing are only some of the possibilities of sewage treatment plant design that might make it easier for the operator to combat occasional adverse effects of plating wastes. There undoubtedly are others. The present state of knowledge of the subject is so nebulous that quantitative design factors generally cannot be suggested. Each problem must be evaluated individually. Serious consideration should be given to advance research to provide quantitative design data for individual situations.

This discussion has been developed from the viewpoint of new sewage plant design. The principles presented in this connection

offer the operator of an existing plant clues to methods that may be tried, within the limits of available facilities, to minimize adverse effects of plating wastes.

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